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The use of red mud as an immobiliser for metal/metalloid-contaminated soil: A review

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Abstract: This review focuses on the applicability of red mud as an amendment for metal/metalloid-contaminated soil. The varying properties of red muds from different sources are presented as they influence the potentially toxic element (PTE) concentration in amended soil. Experiments conducted worldwide from the laboratory to the field scale are screened and the influencing parameters and processes in soils are highlighted. Overall red mud amendment is likely to contribute to lowering the PTE availability in contaminated soil. This is attributed to the high pH, Fe and Al oxide/oxyhydroxide content of red mud, especially hematite, boehmite, gibbsite and cancrinite phases involved in immobilising metals/metalloids. In most cases red mud amendment resulted in a lowering of metal concentrations in plants. Bacterial activity was intensified in red mud-amended contaminated soil, suggesting the toxicity from PTEs was reduced by red mud, as well as indirect effects due to changes in soil properties. Besides positive effects of red mud amendment, negative effects may also appear (e.g. increased mobility of As, Cu) which require site-specific risk assessments. Red mud remediation of metal/metalloid contaminated sites has the potential benefit of reducing red mud storage and associated problems.

Keywords: Bauxite residue; Microbiological response; Mobile metal fraction; Plant response; Soil remediation

1. Introduction

Red mud (also called bauxite residue) is a by-product of alumina production from bauxite by the Bayer process [1]. The Bayer process involves washing bauxite in a hot solution of sodium hydroxide (NaOH) which leaches the aluminium from the bauxite. Development of the process was largely responsible for the major expansion of the industry during the 20th century and it currently underpins over 95% of alumina production globally [2]. The basic chemistry and operational steps of a contemporary Bayer plant are fundamentally the same as described in Bayer's patents in 1887. The chemical and physical properties of red mud depend primarily on the bauxite mineralogy and, to a lesser extent, the effect of the Bayer process on it [3]. The main processes in a Bayer plant which affect red mud production and composition are bauxite milling, pre-desilication (to react silica-containing minerals so as to reduce the time of the digestion stage), digestion with NaOH, clarification, and washing [4]. Red mud comprises the solids remaining after separation from the green liquor after digestion [4].

Red mud is produced in enormous quantities that require safe disposal [5]. Power et al. [4] estimated the annual production of red mud as 120 million t and a global inventory of over 2.6 billion t in 2007. Based on data for annual alumina production (Fig. 1a) it can be inferred that production of red mud has generally increased from 1998 to 2015. Since 2-3 t of bauxite

are used in the Bayer process to produce 1 t of alumina, the amount of red mud produced can be estimated by applying a mean ratio of 1.5 to alumina production data [4], yielding approximately 170 million t of red mud produced worldwide in 2015. Red mud production is expected to increase further in the future since, due to initial exploitation of the highest quality bauxite reserves, the grade of bauxite ore is decreasing, resulting in an increased ratio of red mud production to bauxite [6]. Recently global alumina production has been driven by production in China (Fig. 1a). In 2015 China, Oceania and South America accounted for 50.4%, 18.6% and 11.6% of the global production of alumina, respectively, with the rest of the world accounting for about 20% of production (Fig. 1b). In 2011 annual red mud production in China was 42.6 million t of which 5.2% was reused [7], and in 2013 it reached 73 million t of which 2.9 million t was utilised (4% of the production amount) [6]. The total inventory of red mud deposited in China over time was estimated to be more than 300 million t by 2013 [6].

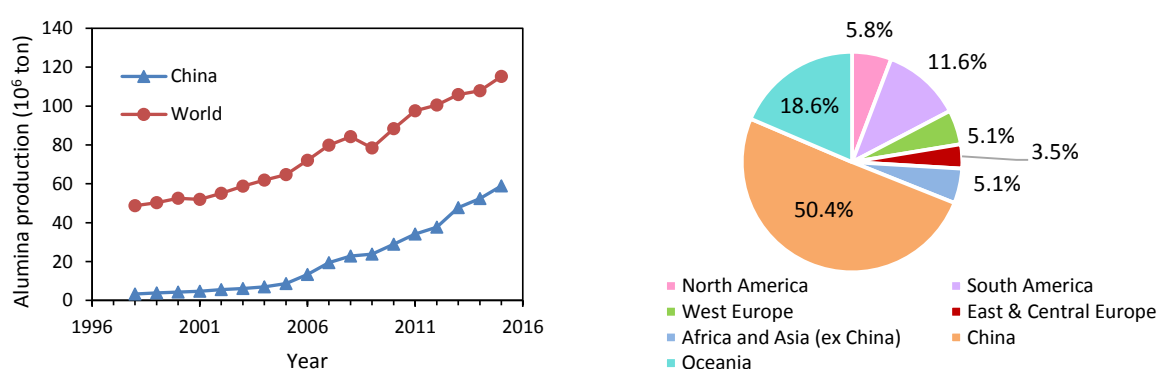


Fig. 1. (a) Annual alumina production worldwide and in China. Global data from International Aluminium Institute [8]. Data for China from National Bureau of Statistics of China [9]. (b) Regional distribution of alumina production in 2015. Data from International Aluminium Institute [8].

The composition of red mud varies depending upon the quality of the ore and processing methods [10-13]. On average, red mud dry mass contains large amounts of Fe_2O_3 (41%) and Al_2O_3 (17%), smaller amounts of SiO_2 (10%), TiO_2 (9%), CaO (9%) and Na_2O (5%), trace elements (e.g. Cr, Cu, Pb, V and Zn) and naturally occurring radionuclides (U, Th isotopes and their daughters, and ^{40}K) [2, 13-16]. Due to washing with NaOH red mud has a high pH (9 to 13) and electrical conductivity (EC) ranging from 0.67 to 60.8 mS cm^{-1} [5, 11, 17-23]. Currently, red mud is treated as a waste and is typically stored in large lagoons or in land-based disposal pits, depending on the method of bauxite processing [14]. The original water content of red mud is more than 80% [24]. Additional thickening or filtration of the slurry are applied in order to store red mud as dry stacks (45–52% water content) or dry cake (<35 % water content) to minimise the land area required for storage [4]. Storage of large volumes of red mud in lagoons can lead to environmental disaster caused by high rainfall and/or failure of the containment structure [4, 14]. The most serious accident [25] involving red mud was on 4 October 2010, when the western dam of the red mud reservoir at an alumina plant in Ajka (Hungary) collapsed. The red mud release killed 10 people and injured more than 100. In addition, rivers and land were contaminated across a large area, with an estimated 800 ha of agricultural land covered by a red mud layer 5-10 cm deep [25]. Other accidents involving red mud have been reported in other countries [26, 27]. Li [28] identified 51 red mud pollution incidents distributed across 20 countries on 5 continents from 1900 to 2012, with

the majority occurring since 1950. These numbers are expected to be an underestimate as not all red mud pollution incidents are reported.

Although the safe disposal and storage of red mud is an international issue and has been extensively researched, better solutions to the storage of red mud and the risks it poses are to reuse red mud. Red mud should be considered a valuable material instead of a waste since it has many potential reuse applications. The abundance of red mud has led to extensive research into possible uses [12]. These include: recovery of Al, Fe, and rare earth metals [29, 30]; a sorbent for treatment of contaminated water [31, 32]; sequestration of CO₂ [33]; an additive to ceramics and building materials [34, 35]; embankment construction [36]; and soil amendment [2, 12, 14, 17, 37-42]. All of these uses may play a role in reducing the storage of red mud.

More recently, various industrial residues have been considered for their potential as amendments for the remediation of contaminated soils characterised by high concentrations of metals/metalloids and low pH [43]. The remediation of metal-contaminated soil is often difficult and expensive, and one cost-effective and feasible option is reduction of risk by metal fixation [44, 45]. In situ fixation of metals is based on the reduction of metal mobility and availability which can be achieved by applying soil amendments [38, 46]. Consequently, the detrimental effects of metals to environmental receptors such as microorganisms, plants, animals, water bodies and humans are reduced [43]. Whilst red mud represents a disposal problem worldwide due to its high concentrations of potentially toxic elements (PTEs), it has a large specific surface area suitable for remediation of metal-contaminated substrates [37]. In recent years red mud has been added to contaminated soils, mainly resulting from mining activities, to neutralise low pH and reduce metal mobility through different physicochemical mechanisms [44, 47]. These include immobilisation of metals through adsorption and surface complexation with Fe oxides and formation of inner sphere complexes with Fe and Al oxides and hydroxides [47, 48].

A number of studies have reported on the application of red mud from different sources for amending contaminated soil, and the mobility of different PTEs, mainly metals and metalloids, has been investigated globally [37, 38, 46, 49-52]. Furthermore, increasing numbers of field experiments have been conducted utilising red mud to amend contaminated soils, in which a range of plants have been grown for human consumption, from fodder crops to corn and vegetables [38, 45, 49, 53, 54]. There is also improved understanding of the remediation mechanisms and response of microorganisms in soils amended with red mud. Although several review papers mention soil remediation using red mud [2, 55-57] and Cappuyns [58] provides an overview of red mud as an amendment for metal/metalloid immobilisation, mainly general results are stated, such as relating to the efficiency of remediation and reduction of phytotoxicity, without widespread review and more in-depth analysis. This review aims to provide a comprehensive understanding of the role of red mud as a soil amendment by considering numerous laboratory and field studies which have investigated PTE fixation and the response of plants and microorganisms to red mud amendment of contaminated soil. Based on this, the review also identifies the key characteristics of red mud to be considered in evaluating its suitability for remediation of contaminated soil.

2. Properties of red mud related to the potential risks as a soil amendment

Red muds vary in composition because of differences in bauxite composition and the operation of the processing plant [2]. Red mud is strongly alkaline, with a reported pH ranging from 9.0 to 13.1, a result of the reaction of NaOH with the bauxite ore in the Bayer process. Due to incomplete washing of the residue material before disposal, NaOH, sodium carbonate (Na_2CO_3) and sodium aluminate ($\text{NaAl}(\text{OH})_4$) remain in red mud, giving the material its highly alkaline nature [59]. Since red mud itself also contains PTEs this characteristic cannot be neglected when using red mud as a soil amendment. Therefore the environmental risk posed by the composition of red mud should be considered before using it for the remediation of contaminated soils.

2.1. PTE concentrations and mobility in red mud

Reported concentrations for each metal/metalloid (Table 1) vary considerably reflecting the different sources of red mud. For example, Cu, Pb and Zn concentrations were up to 301 mg kg^{-1} , 332 mg kg^{-1} and 670 mg kg^{-1} , respectively, in some red muds, but in others were below the limit of detection. Cr concentrations varied from 193 to 1377 mg kg^{-1} and had the highest mean value of all contaminants, except for V. Due to the elevated Cr concentration in one red mud used in a field study (1377 mg kg^{-1}), soil total Cr concentration increased from 45 mg kg^{-1} before amendment to $63\text{-}135 \text{ mg kg}^{-1}$ after addition of 5% w/w red mud [38]. Cd concentrations in red mud were low, compared to other elements, and were generally less than 5 mg kg^{-1} . Nevertheless, As and Cd are common components of red mud and are highly toxic, even at low concentrations, and thus pose a hazard to ecosystems and human health. Vanadium is another common component of red mud but its toxic effects are less well known compared to other contaminants. Vanadium concentration in soils around the world ranges from trace amounts to 400 mg kg^{-1} , with a mean of 150 mg kg^{-1} [60]. The US Environmental Protection Agency (USEPA) has not listed V as a pollutant requiring urgent research and legislation. However, in a few countries standards and regulations have been set for the maximum allowable V concentration in agricultural soil, for example, 150 and 130 mg kg^{-1} in Russia [60] and Canada [61], respectively. Furthermore, application of red mud to soil could increase labile V by 18-76% [62]. The highest V concentration reported in red mud in Table 1 is 4220 mg kg^{-1} , which suggests that high V concentrations could restrict the use of red mud as a metal/metalloid immobiliser for soil in which crops are grown for animal or human consumption.

Table 1. Red mud pH and total metal/metalloid concentrations (mg kg⁻¹ dry weight) and country of production as reported in the literature. Summary statistics for red mud composition and EU limits for metals/metalloids in sludge for application to agricultural land are stated at the foot of the table.

Red mud number	pH	As	Cd	Cr	Cu	Hg	Ni	Pb	V	Zn	Method of total metal/metalloid determination	Country of production	Reference
1	12.5			415				182		41	XRF	China	[11]
2		53	<LOD	246	<LOD		<LOD	102	384	80		China	[29]
3			<LOD		301			119		91	Digestion using HNO ₃ and H ₂ O ₂	China	[49]
4		11	0.80	388	91	0.46	51	94		56	XRF	China	[63]
5	12.9	125		848	182		169	332	4220	670	Digestion using HNO ₃ , H ₂ O ₂ , HCl	China	[64]
6	12.6	<LOD						72		55	Digestion with HCl, HNO ₃ , HClO ₄	China	[51]
7		119		518	76		59	61	3185	283	XRF	China	[64]
8	12.7		0.08					18		74	Digestion with HNO ₃ , HClO ₄ , HF	China	[65]
9	11.3	62	2.1		6.8			78		61	Digestion with aqua regia	Korea	[46, 66, 67]
10			0.04	395	41		<LOD	20		<LOD	Digestion using HNO ₃ and H ₂ O ₂	India	[68]
11	9.0	47	0.77	193	49		112	63		78	Digestion with aqua regia	Hungary	[14]
12	13.1	196		864	104		361	215	1132	162	XRF	Hungary	[19]
13	10.2			430	55	<0.2	215	174		130	Digestion with aqua regia	Hungary	[37]
14	10.5		8.2	449	84		246	175		151	Digestion with aqua regia	Hungary	[43]
15	10.4	49	4.1		183			158		334	Digestion with aqua regia	Hungary	[45]
16	10.7	131	2.0		72			152		142	Digestion using HNO ₃ and H ₂ O ₂	Hungary	[52]
17	10.4		4.1		183			158		334	Digestion with aqua regia	Hungary	[53]
18	10.2	128	1.5	435	90		26	91	1010	102	Digestion with aqua regia	Hungary	[62]
19	10.5				84			8.2		151	Digestion with aqua regia	Hungary	[69]
20	11.1	<LOD	1.5		5.7			49		<LOD	Digestion using HNO ₃ and HCl	Italy	[70]
21		20	0.70	300	50		25	50	300	25	Digestion with HNO ₃ , HClO ₄ , HF	Italy	[71]
22	11.5		<LOD	790	24			<LOD	649	0.02	Digestion using HNO ₃ and HCl	Italy	[50, 72, 73]
23	11.5		<LOD					13		5.2	Digestion using HNO ₃ and HCl	Italy	[74, 75]
24	10.7	62	23	1237	35	0.70		144	1476	506		Italy	[76]
25	10.2		18	1377	52		79	84		155	Digestion with aqua regia	UK	[38]
26	12.2	173	<1		48			184		158	Digestion using HNO ₃ and H ₂ O ₂	UK	[52]
27	10.8	36	6		4			58		36	Digestion with aqua regia	UK	[77]
28			0.37	604	71			1.1		56	Digestion with HClO ₄ and HNO ₃	Romania	[78]
29	12.1		<LOD	380	69		15	49		24		Romania	[79]
30	11.6		4.0		50			53		91	Digestion with aqua regia	Romania	[80]
31	10.2	1.0	1.3	1350	52	0.30	80	50		80	Digestion using HNO ₃ and HF	Spain	[15]
32		152	86	205	160					161	XRF	Brazil	[81]
33	12.0		33		38			51		31		Canada	[82]
34	11.4			633	9			43		20		Canada	[83]
35	9.4	75	34	860	48		342	109		270	Digestion with HF, H ₂ SO ₄ , HClO ₄	USA	[5]
36	10.5	11	7.2	441	66		5.6	49		12	Digestion with HF, H ₂ SO ₄ , HClO ₄	USA	[5]
37							31		730	20		Australia	[84]
38	9.8	248			32		1.8	39		8.5	Digestion with aqua regia	Australia	[85]
mean ^a	11.1	83	8.5	607	73	0.37	101	92	1454	122			
median ^a	10.8	122	6.6	445	55	0.58	80	75	1010	97			
min	9.0	1.0	<LOD	193	<LOD	<0.2	<LOD	<LOD	300	<LOD			
max	13.1	248	86	1377	301	0.70	361	332	4220	670			
n ^b	29	22	28	22	33	4	18	36	9	38			
Limits ^c			20-40		1000-1750	16-25	300-400	750-1200		2500-4000			

Notes: LOD - limit of detection, XRF - X-ray fluorescence spectroscopy; spaces for pH and PTE concentrations mean no values were reported in the literature; spaces for method mean that it was not specified. ^a <values and <LOD are treated as zero as LOD values not always specified. ^b Number of data points for calculating summary statistics. ^c Maximum permissible PTE concentrations in sludge for use in agriculture in the EU [86]. Note that limit values are not stated for As, Cr and V.

There is currently no specific guidance or legislation regarding the application of red mud for remediating contaminated soil. However some existing legislation may be relevant for

evaluating the suitability of red mud for soil remediation based on its total metal content, such as legislation governing sewage sludge application to land. For example, the European Commission Sludge (Use in Agriculture) Directive [86] includes not only limit values for metal concentrations in sludge for use in agriculture, but maximum permissible average annual rates of addition of PTEs over a 10-year period. The limit values for Cd, Cu, Hg, Ni, Pb and Zn are shown at the bottom of Table 1. The only reported PTE concentrations in red mud in Table 1 exceeding the permissible values were for Cd at one location whilst all other reported values were below these limits. However it should be noted that these maximum permissible values are for application to agricultural land, rather than to PTE-contaminated soil.

The mobility of PTEs is of great importance in understanding the effects of applying red mud to soil. Mobility varies between different PTEs and in red muds from different sources, as demonstrated here by some examples from the literature. Rubinos and Barral [15] investigated the mobility of PTEs in red mud using the sequential extraction procedure of Tessier et al. [87]. The fraction of ‘potentially mobile’ metal was very low for Cr, Ni, Pb and Zn (<0.6%), which suggests that these metals are strongly fixed in red mud and their leaching potential is very low. Similarly, Kutle et al. [88] reported an almost negligible fraction (~0.2%) of exchangeable Cr at pH 7 in red mud from Croatia, but this increased to 48.4% at pH 3.5[88], indicating the critical role of pH in the mobility of Cr in red mud. In contrast, in another study higher proportions of Cd and Cu were potentially mobile, 20% and 4%, respectively [15]. The mobility of PTEs in red mud may increase after soil amendment, due to a decrease in pH of the red mud induced by addition to soil with a lower pH. However, the pH of the soil environment is seldom as low as the pHs used in some of these extraction experiments (pH 2-3.5) so the risk of increasing PTE mobility in red mud after soil amendment is expected to be low, but should be evaluated on a site-specific basis.

2.2. Sodium content and salinity of red mud

Red mud has a high salt content and EC, dominated by sodium (Na^+) [89], with soluble Na concentrations reported of up to 6090 mg kg^{-1} [79]. The addition of red mud has been shown to cause a significant increase in exchangeable Na in soil. When red mud was added at 4% w/w to soil the exchangeable Na concentration increased from 0.11 g kg^{-1} to 2.41 g kg^{-1} [74]. In another experiment the EC of soil increased from 0.49 mS cm^{-1} to 1.48 mS cm^{-1} 6 months after red mud addition [74].

Higher application rates of red mud may increase the effectiveness of remediation of contaminated soils. However, the extremely high Na content in red mud may cause a potential salinity problem in the remediated soil, particularly if red mud additions continue over a period of time so that salinity accumulates in the soil. In addition, whilst pre-treatment of red mud by seawater could improve the effectiveness of red mud addition for immobilising some metals in contaminated soil, this pre-treatment could also increase the EC of red mud. For example, Udeigwe et al. [5] reported that the EC of red mud treated with seawater increased from 6.34 to 21.0 mS cm^{-1} . Consequently, the soil amended with this neutralised red mud at 2% w/w rate had an EC of 0.44 mS cm^{-1} , higher than the soil amended with non-neutralised red mud (0.35 mS cm^{-1}).

2.3 Radiological properties of red mud

The radionuclide content of red mud is another concern for soil application, although few

studies have focused on this aspect. Reported ranges of ^{232}Th , ^{226}Ra and ^{40}K radioactivity in red mud were 87-555, 150-700 and 5-583 Bq kg⁻¹, respectively [1, 90-92]. Whilst not involving amendment of a metal-contaminated soil, in a field study of red mud addition to sandy soils, ^{228}Th increased from 8 Bq kg⁻¹ in the unamended control soil to 13 and 71 Bq kg⁻¹, in soils with 60 and 480 t ha⁻¹ red mud application rates, respectively [91]. However, the corresponding activity concentrations of ^{228}Th in lettuce were 1.9, 1.8 and 3.3 Bq kg⁻¹ respectively, suggesting the radionuclide uptake by lettuce was less influenced by red mud application [91]. In a study of radiological consequences of amending sandy soils with red mud, Summers et al. [93] reported that at rates of soil amendment below 1500 t ha⁻¹ (~40% w/w, for application depth to 0.25 m and assuming 1.5 t m⁻³ soil bulk density), any increase in γ radiation exposure would not exceed the recommended increment above background radiation dose for the general public of 1 mSv year⁻¹ [94]. However, more research is needed to assess the long-term effects related to radionuclides after land application of different sources of red mud.

3. Remediation of contaminated soil with red mud

The negative effects of metal-contaminated soil can be summarised as risk for the health of humans and animals, reduction of plant growth, and influence on microorganisms [53, 95]. The effectiveness of red mud remediation of soil should be evaluated based on these aspects. The mobility of metals in the soil is of great importance for metal transformation and consequently for human and environmental health, and can be evaluated by different chemical extractants [96]. A direct way to identify metal/metalloid bioavailability and plant growth after red mud application is cultivating plants in pot or field experiments [38, 45, 53, 97]. In addition, the functionality, composition and diversity of the soil microbial community has been proposed as a sensitive early indicator of soil ecological stress and could be used to evaluate the effectiveness of red mud remediation [39, 46, 75]. In this section the effects of red mud amendment of metal/metalloid-contaminated soils are assessed with respect to metal mobility as measured by chemical extraction, plant growth and PTE concentrations in plant tissues, and soil microbiological properties. The processes underlying the reported effects are evaluated where possible.

3.1. Behaviour of PTEs in red mud-amended soil

3.1.1. Influence of red mud amendment on extractable metals and metalloids in soil

The remediation of contaminated soil by metal fixation with red mud is a complex subject that has received wide coverage in the literature and is still an important topic of research. Many studies report reduced chemical extractabilities of metals after addition of red mud to contaminated soil [14, 37, 38, 49, 51, 52, 66]. One of the main approaches to studying the behaviour of metals/metalloids in contaminated soil is using chemical extractants. Table 2 summarises the results of metal/metalloid extractability in studies of soil remediation with red mud, identified in searches of the 'Web of Science' database. The focus of the table is studies using single chemical extractants. The results of studies using sequential chemical extractants to identify the effects of red mud amendment on metal/metalloid speciation in contaminated soils are reviewed in Section 3.1.3.

Table 2. Summary of studies assessing the effect of red mud on metal/metalloid mobility in soil using single chemical extractants.

Red mud application rate (% w/w) and red mud number in Table 1	Soil source	Initial soil pH and total metal/metalloid concentration (mg kg ⁻¹)	Soil cation exchange capacity (CEC) (cmol kg ⁻¹), texture and organic C (OC) or organic matter (OM) (g kg ⁻¹)	Red mud pH and total metal/metalloid concentration (mg kg ⁻¹)	Study scale and remediation time (days - d)	Method of metal/metalloid extraction	soil pH value and % change in soil pH and extractable metal/metalloid concentration after red mud application (%)	Reference
2% 16	Agricultural grassland, near former As and Cu ore mine and smelter, Devon, UK	pH: 4.6 As: 4772 Cu: 1058	CEC: 8.3 Sand: 54.6% Silt: 34.8 % Clay: 0.6 %	pH: 12.2 As: 48.0 Cu: 173	Lab 70 d	0.05 M (NH ₄) ₂ SO ₄ for As, 1 M NH ₄ NO ₃ for Cu	Soil pH: 5.7 (+24) As (-28) Cu (-76)	[52]
5% 13	Derived from a Cu smelter site, Brixlegg, Austria	pH: 7.2 Cd: 4.1 Cr: 26 Cu: 760 Ni: 36 Pb: 431 Zn: 991	CEC: 11.1 Sand: 41.7% Silt: 45.7% Clay: 12.6% OC: 50	pH: 10.2 Cd: <10 Cr: 430 Cu: 55 Ni: 215 Pb: 174 Zn: 130	Lab 100 d	1 M NH ₄ NO ₃	Soil pH: 7.5 (+4.0) Cd (-33) Cr (0) Cu (+47) Ni (-22) Pb (-80) Zn (-53)	[37]
2% 5% 9	Munbaek gold mining area, Chungbuk Province, Korea	pH: 4.6 As: 20.0 Cd: 2.5 Pb: 117 Zn: 233	CEC: 11.8 Sand: 65.9% Silt: 20.2% Clay: 14.0%	pH: 11.3 As: 62.3 Cd: 2.1 Pb: 78.2 Zn: 60.6	Lab 40 d	0.1 M Ca(NO ₃) ₂	2% red mud: Soil pH: 8.1 (+76) As (-68), Cd (-89) Pb (-96), Zn (-98) 5% red mud: Soil pH: 9.4 (+103) As (-29), Cd (-98) Pb (-99), Zn (-99)	[66]
1% 2% 5% 6	Farmland polluted due to a tailing dam collapse, Guangxi Zhuang Autonomous Region, China	pH: 3.7 Pb: 817 Zn: 614	CEC: 11.2 OM: 24.2	pH: 12.6 Pb: 71.7 Zn: 55.1	Lab ~90 d	0.1 M CH ₃ COOH	1% red mud: Soil pH: 5.9 (+60) Pb (-34), Zn (-52) 2% red mud: Soil pH: 6.6 (+78) Pb (-55), Zn (-60) 5% red mud: Soil pH: 6.8 (+83) Pb (-74), Zn (-67)	[51]
2% 5% 1	Agricultural area downstream of former Pb and Zn ore mine in Gyöngyösorszi, Hungary	pH: 6.9 As: 122 Cd: 8.9 Pb: 440 Zn: 1601	NA	pH: 9.0 As: 47.4 Cd: 0.77 Pb: 63.0 Zn: 77.5	Lab Mean of 5 samples (after 10 d, 20 d, 61 d, 182 d, 730 d)	0.2 M CH ₃ COONH ₄	2% red mud: Soil pH: 7.0 (+1.5) As (-49), Cd (-1.0) Pb (-15%), Zn (-22%) 5% red mud: Soil pH: 7.2 (+4.3) As (-59), Cd (-11) Pb (-43), Zn (-42)	[14]
2% 11	Mine wastes from Pb and Zn extraction, Jasper County, Missouri, USA	pH: 5.9 Cd: 92 Cu: 64 Pb: 5022 Zn: 18532	CEC: 0.3 Sand: 76% Silt: 22% Clay: 2% OC: 1.2	pH: 10.8 Cd: 6 Cu: 4 Pb: 58 Zn: 36	Lab ~118 d	1 M NH ₄ NO ₃	Soil pH: 7.3 (+24) Cd (-29) Cu (-9.6) Pb (47) Zn (-77)	[77]
3%, 5% 25	Adjacent to decommissioned Zn/Pb smelter at Avonmouth, UK	pH: 4.7 Cd: 79 Cu: 311 Ni: 36 Pb: 4210 Zn: 3970		pH: 10.2 Cd: 18 Cu: 52 Ni: 79 Pb: 84 Zn: 155	Field 760 d	1 M NH ₄ NO ₃	3% red mud: Soil pH: 5.6 (+20) Cd (-17), Cu (-83) Ni (-15%), Pb (-55) Zn (-42) 5% red mud: Soil pH: 6.5 (+38) Cd (-52), Cu (-93) Ni (-57), Pb (-82) Zn (-75)	[38]
1% 17	Near Pb/Zn smelter closed in 1992, Arnoldstein, Austria	pH: 4.9 Cd: 5.6 Pb: 913 Zn: 545	CEC: 5.0	pH: 10.4 Cd: 4.1 Pb: 158 Zn: 334	Field 1095 d	1 M NH ₄ NO ₃	Soil pH: 5.7 (+16) Cd (-90) Pb (-90) Zn (-88)	[53]
0.5% 1% 3	Agricultural area contaminated due to wastewater irrigation, Hunan province, China	pH: 5.4 Cd: 0.89	CEC: 18.8 OM: 45.2	Cd less than detection	Field ~55 d	0.05 M EDTA-Na ₂	NA 0.5 red mud: Cd (-11) 1% red mud: Cd (-19)	[49]
1% 30	Copsa Mică, near former Zn smelter, Romania	pH: 5.5 Cd: 13.0 Pb: 608 Zn: 882	NA	pH: 11.6 Cd: 4.0 Pb: 52.5 Zn: 91.3	Field 2191 d	1 M NH ₄ NO ₃	Soil pH: 7.6 (+38) Pb (-99) Zn (-97) Cd (-86)	[80]

Notes: - decrease compared with the control, + increase compared with the control, 0 no change compared with the control. NA, information not available. All increases or decreases are compared to unamended contaminated control soils.

Before examining the effect of red mud amendment of contaminated soils, it is important to recognise that soils are variable and complex environmental media, both structurally and compositionally [37]. Furthermore, the specific characteristics of red muds from different sources also vary, although the main constituents are generally similar [22, 98]. Nevertheless, some common patterns can still be identified in the remediation of soils with red mud. Overall metal mobility appeared to be lower in soils amended with red mud compared to control soils even when different extractants were used (Table 2). For example, in a field study NH_4NO_3 -extractable Pb decreased by 90% with 1% w/w addition of red mud despite the high initial soil total Pb concentration (913 mg kg^{-1}) [53]. The highest decrease in % extractability reported in any study was 99% for Pb and Zn [66] and 99% for Pb [66] with red mud application rates of 5% and 1%, respectively.

Due to variability in the results of different studies it is difficult to identify which metals are more effectively remediated by red mud amendment of contaminated soils. In some cases red mud amendment increased metal mobility in the soil, especially for As and Cu. For example, 5% (w/w) red mud addition reduced labile concentrations of Cd, Ni, Pb and Zn, by 33%, 22%, 80% and 53%, respectively, whilst labile As and Cu concentrations increased by 24% and 47%, respectively [37]. In another study using DGT (diffusive gradients in thin films) to detect bioavailable metal/metalloids in soil solution, the flux of Cu from the soil solid phase to solution was shown to be significantly higher in red mud-amended contaminated soil compared to unamended controls, whilst Ni and Zn fluxes were significantly lower [43]. Increased mobility of Cu in red mud-amended soil compared to untreated contaminated soil has been attributed to increased dissolved organic carbon (DOC) in the amended soil since Cu tends to be strongly absorbed to organic matter (OM) [43]. The increased mobility of As reported in [37] was related to increasing soil pH, which results in decreased adsorption of As(III) and As(V) to goethite [99]. Although, in some cases, red mud addition may increase the mobility of metal and metalloid soil contaminants, overall, the studies to date demonstrate the potential of using red mud to remediate metal/metalloid-contaminated soil and thereby utilise red mud waste. More detailed discussion of mechanisms affecting metal immobilisation by red mud is contained in Section 3.1.5.

3.1.2. Effect of red mud application rate on metal and metalloid mobility

The application rate of red mud is an important consideration in the remediation of metal/metalloid-contaminated soil. As the application rate of red mud increased, metal extractability tended to decrease in both laboratory and field-scale experiments (Table 2). For example, the percentage decreases of Pb extractability were 34%, 55% and 74% with red mud application rates of 1%, 2% and 5%, respectively [51]. Similarly, in a field experiment, increasing addition of red mud was also accompanied by decreasing metal extractability; for example, for Zn the decrease in extractability compared to unamended soil was 42% after 3% red mud addition and 75% after 5% red mud addition [38].

However, in some cases, increasing red mud addition was not beneficial for improving the immobilisation of metals. For example, the percentage decrease in extractable As compared to unamended soil changed from 68% to 29%, as the application rate of red mud increased from 2% to 5% [66]. However, this result can be attributed to the much higher As content in the red mud (62.3 mg kg^{-1}) compared to the initial soil (20.0 mg kg^{-1}). Friesl et al. [37] suggested that the disadvantages exceeded the advantages when the red mud addition rate to contaminated soils is 5% (w/w) or higher since reduced lability of Cd, Ni, Pb and Zn is offset by increased lability and solubility of As, Cu, Cr and V in soil. They concluded that application rates should be adjusted according to soil conditions (e.g. pH) and, in some cases,

it may be necessary to lower the concentrations of pollutants contained within the red mud using leaching procedures before addition to contaminated soil. Consequently, the application of red mud to reduce metal/metalloid mobility in contaminated soils should be carried out only after determination of red mud properties to assess the potential risks of amendment.

3.1.3. Effect of red mud addition on metal and metalloid “speciation”

Speciation in this review is determined by operationally defined fractions in that the metal/metalloid phases are determined according to a given procedure and the actual determinations correspond to extractable element contents rather than well-defined species. To improve understanding of the function of red mud in soil remediation, sequential metal extractions have been conducted in many studies to investigate the distribution of PTEs among different soil fractions [43, 44, 50, 51, 66]. From these studies, including both laboratory and field experiments, the high Fe oxide content of red mud appears to be primarily responsible for the immobilisation of the majority of metals/metalloids, as illustrated with some examples below from the literature.

In pot experiments, after application of 2% w/w red mud to soil contaminated by sewage sludge application, the fractionation of metals/metalloids in the treated soil changed significantly compared to the unamended control soil [43]. The exchangeable concentrations of Cu and Ni in the red mud-treated soil decreased by 52.7% and 58.8%, respectively, and were significantly lower than in the unamended soil. Concentrations of Cd, Cu and Zn occurring in the Fe/Mn oxide fraction increased significantly compared to in the unamended soil, whilst Cu concentrations in the carbonate- and organic matter-bound fractions were significantly lower than in the unamended soil [43]. Other laboratory studies have also reported decreased exchangeable metal/metalloid concentrations in contaminated soils amended with red mud. In a study using topsoil from a gold mining area, the exchangeable fractions of Cd, Pb, and Zn in soil amended with 2% red mud were reduced by 43.9%, 98.4%, and 92.6%, respectively, compared to the control soil [66]. In soil contaminated by deposition from a Pb/Zn smelter, red mud additions of 5% and 10% resulted in significantly lower acetic acid extractable (exchangeable) Pb and higher % residual Pb compared to unamended soil after 12 months incubation [100]. Similarly, in a 28-day laboratory study in which 20% w/w red mud was incubated with mine tailings, mobile Cd, Pb and Zn fractions in soils amended by red mud were converted to the less mobile Fe/Mn oxides fraction along with slight conversion to the residual fraction, due to formation of surface complexes with Fe/Al (hydr)oxides [48]. These findings have been replicated in a longer-term study involving 1% addition of red mud to field plots near a former Pb smelter [80]. Five years after red mud addition, the Zn concentration in the mobile soil fraction in the treated soil (18.7 mg kg⁻¹) was significantly lower than in the unamended soil (557 mg kg⁻¹), with redistribution of soil Zn to crystalline Fe oxides (up to 13.3%), amorphous Fe oxides (up to 12.6%) and the residual fraction (up to 9%) [80]. In the case of Cd, application of red mud also reduced the mobile fraction to 12.6% compared to 76.6% in the unamended soil, and the other Cd fractions increased due to the redistribution of the mobile fraction bound to Mn oxides (from 3.8 to 11.1%), bound to amorphous Fe oxides (2.6 to 9%) and bound to crystalline Fe oxides (from 3.8 to 7.1%) [101].

To assess changes in As distribution in soils amended with red mud the sequential extraction procedure for As proposed by Wenzel et al. [102] has been widely used. Garau et al. [50] used this procedure to assess As mobility and found reduced water-soluble As in soil amended with red mud compared to the control soil (3.44% and 5.59% of total As, respectively) and a substantial increase of the residual (non-extractable) As fraction (>300%

compared to the control soil), resulting in decreased bioavailable As. The application of red mud has also been shown to shift the As distribution from the non-specifically sorbed fraction to the Fe- and Al-bound fraction [66].

3.1.4. Effect of red mud addition on the chemical characteristics of soils

The alkaline nature of red mud resulted in increased soil pH in all the case studies in Table 2, by 0.1 to 4.8 pH units in the red mud-amended contaminated soils in comparison with control unamended soils. Most of the soils are acidic, and an increase of soil pH to near neutral should be helpful not only for metal immobilisation but for plants and soil microorganisms. However, Lee et al. [66] reported an increase in soil pH to 9.4 after addition of 5% w/w red mud.

Several studies have reported an effect of red mud amendment on soil carbon (C). In a contaminated mining soil 2 years after 4% red mud amendment, total organic C (TOC) was 20.1 g kg⁻¹ dry weight compared to 34.9 g kg⁻¹ in the unamended control soil, and water-soluble C was 2.18 g kg⁻¹ and 0.99 g kg⁻¹, respectively [50]. Similarly, DOC in pore waters of two soils increased after 2% red mud amendment, from 42.8 to 66.7 and from 71.8 to 87.6 mg kg⁻¹ [43]. In other remediation studies with red mud, it was found that the combined effect of the red mud alkalinity and high Na content enhanced the release of DOC/water-soluble C from the amended soil OM [73, 100, 101]. DOC compounds can decrease the sorption of Cu and Pb onto soil surfaces, mainly by forming soluble organo-complexes or being preferentially adsorbed onto surfaces instead of metals [38, 103]. Gray et al. [38] found that the effect of DOC on soluble Cu and Pb is likely only transitory, because the increase in soluble Cu and Pb was only observed in the first few months after amendment and was not apparent after 21 months [38].

Increased soil EC as a result of red mud addition has been reported in many studies [5, 43, 46, 73, 74, 77, 100, 104]. Compared with the control soil, the EC of soil after 2% red mud addition increased by 24% to 434% in different case studies [5, 43, 46, 77]. Soil EC also increases with increasing red mud application rate. For example, in 40-day pot equilibration experiments, EC for soils from the Munbaek gold mining area, Korea, contaminated with As 20 mg kg⁻¹, Cd 2.4 mg kg⁻¹, Pb 116 mg kg⁻¹ and Zn 233 mg kg⁻¹, increased from 0.151 mS cm⁻¹ in the control soil to 0.457 and 0.638 mS cm⁻¹ after 2% and 5% w/w red mud additions, respectively [66].

3.1.5. Key controls on metal and metalloid immobilisation by red mud addition

A number of factors control the effectiveness of red mud amendment for metal immobilisation in contaminated soils. Soil pH plays a significant role in metal mobility. In the majority of cases, the metal-polluted soil has a low pH so the addition of red mud increases soil pH and thus reduces metal mobility [38, 51]. The reduction of the labile pool of metals such as Cd, Cu, Pb and Zn is related to increased metal adsorption due to the increasing negative surface charge of soil and precipitation of metal hydroxides and carbonates at high pH [69, 105]. Arsenic mobility responds differently to pH, with experiments conducted in solutions at pH 4, 7 and 10 showing that arsenate adsorption by red mud decreased as pH increased [106]. According to pH_{PZC} measurements [107], at acid pH the surface of soil particles has a net positive charge that attracts H₂AsO₄⁻ ions in solution, while at neutral or alkaline pH, there is a net negative surface charge which repulses HAsO₄²⁻ ions.

Nevertheless, pH change is not the only factor involved in metal/metalloid stabilisation in

soils after red mud amendment, as demonstrated by the second case study in Table 2 in which soil pH increased by only 0.3 [37]. The mineralogy of red mud also plays an important role in the immobilisation of metals due its high Fe, Al and Ca content [14, 98, 108]. Typically, 60% by weight of red mud comprises Fe and Al oxides and oxyhydroxides as hematite (Fe_2O_3), boehmite ($\gamma\text{-AlO}(\text{OH})$) and gibbsite ($\text{Al}(\text{OH})_3$) [106]. Red mud also contains high quantities of cancrinite ($\text{Na}_6\text{Ca}_2[\text{Al}_6\text{Si}_6\text{O}_{24}] \cdot 2\text{H}_2\text{O}$) with a high sorption capacity for metals due to its negative charge density which is neutralised by metal adsorption on external surfaces and by the incorporation of metals of compatible ionic radius in the cages and channels of its internal structure [47]. Hematite, boehmite, gibbsite and cancrinite phases were identified as the probable principal mineralogical phases involved in immobilising metals/metalloids in contaminated soil after red mud amendment [14, 47]. The possible reason for As fixation is inner sphere complexation on the reactive surface of newly formed Fe oxides, i.e. amorphous iron III arsenate ($\text{FeAsO}_4 \cdot \text{H}_2\text{O}$). Consequently, most As(V) sorbed in red mud (about 80%) was strongly and specifically associated with the Fe-Al oxide and oxyhydroxide phases [106]. The decreased concentrations of soluble and extractable As in the amended soils can also be attributed to an increase in the available Ca content due to red mud addition, leading to As immobilisation by sorption or the formation of Ca-As precipitates [66]. Thus, the response of As in contaminated soil to red mud amendment may appear as either immobilisation or mobilisation since the Fe-Al oxide content of red mud acts to immobilise As, while the higher pH may have the opposite effect, resulting in increased As mobility [37, 66].

The stability and longevity of amendments is an important consideration for assessing different treatments for remediating contaminated soil. Results from sequential extractions showed that only low concentrations of Cd, Pb and Zn adsorbed by the red mud were in the form of water-soluble and exchangeable fractions, while the greatest concentrations of the metals adsorbed were tightly bound and would not be expected to be released readily under environmental conditions [47]. Soil acidification can occur on a broad scale such as through atmospheric deposition, and thus the resilience of attenuated metal availability by red mud to acidification should be evaluated. Lombi et al. [69] investigated the effect of pH changes on the lability (the exchangeable fraction) of metals in two metal-contaminated soils treated with 5% red mud, 0.25% lime or 2% beringite (w/w basis) using a modified isotopic dilution technique in combination with a stepwise acidification procedure. Significant decreases in the lability of Cd, Cu and Zn occurred for all amendments, but were most marked for red mud addition. The mean decrease in lability compared with the unamended control soil for red mud were 16.8% (Cd), 29.4% (Cu) and 47.5% (Zn), for lime were 0.9% (Cd), 18.5% (Cu) and 24.8% (Zn) and for beringite 8.4% (Cd), 23.9% (Cu) and 29.8% (Zn). However, when the soils were re-acidified, the labile pool of metals increased sharply in the soils treated with lime and beringite. In contrast, the lability of metals in soil amended with red mud was always lower than that in the untreated soils across the range of pH values tested. These results suggested that the mechanism of action of lime and beringite was similar, mainly through formation of metal carbonates and hydroxides for the fixation of metals. In the case of red mud, the more long-lasting metal fixation may be attributed to a combination of pH dependent and independent mechanisms (possibly solid-phase diffusion or migration into micropores). Similarly, Hamon et al. [109] reported that application of red mud (1% w/w) to a soil contaminated by mine tailings lowered the labile Cd and Zn to 1.6% and 3.6%, compared to 3.2 and 5.9% respectively for the control. Interestingly, it was also observed that the fixation of Cd after red mud addition was more resistant to weak-acid dissolution (pH 6-7) than after the application of lime. These results provide further supporting evidence that the attenuation effect of red mud on metal/metalloid lability in contaminated soils is not

simply a pH effect and that other mechanisms are involved.

3.1.6. The role of red mud pre-treatment

Neutralisation of red mud is recommended to reduce any adverse environmental impact arising from uncontrolled release from storage [110]. Red mud with a pH of 7.0 after treatment with HCl had a decreased capacity to adsorb metals by 30% compared with the untreated red mud with pH 11.5 [47]. The mineralogy of this red mud was changed by acid treatment. Partial dissolution of cancrinite in the acid-treated red mud caused a corresponding increase in other phases, particularly in hematite. Metal speciation was also changed, in particular, the water-soluble and exchangeable metal fractions were higher in the acid-treated red mud than in the untreated red mud. Udeigwe et al. [5] compared neutralised red mud with non-neutralised red mud for the remediation of contaminated manured soils. Interestingly, the red muds neutralised by synthetic seawater had little improvement over untreated muds in reducing water-extractable soil Zn concentration, but reduced release of water extractable Cu, suggesting different mechanisms for the retention of these two metals in the amended soils. In particular the neutralisation process increased the concentrations of the divalent cations, Ca and Mg, which could in turn enhance binding between clay (or metal oxides) and OM. Because most Cu in soil is complexed by OM, as mentioned earlier, the soluble Cu retention was intensified by the OM-clay binding ability resulting in the decrease of Cu mobility [5]. Meanwhile, exchangeable Al^{3+} and Fe^{3+} were replaced by Ca^{2+} and precipitated as $\text{Al}(\text{OH})_3$ and $\text{Fe}(\text{OH})_3$ when soil pH is above 5.5, and these newly formed oxides and hydroxides provide additional sites for sorbing Cu [111]. In contrast, Zn in the manured soils studied [5] is likely in the exchangeable and precipitated forms and would be less likely subjected to the effect of increased OM-clay binding caused by the neutralisation of the red muds. Although the use of neutralised red mud did not increase the immobilisation of all metals measured by Udeigwe et al. [5], the study indicates the possibility of increasing the remediation effectiveness of red mud through pre-treatment. However, this would need to be confirmed by further long-term studies as the duration of the study by Udeigwe et al. was only 48 h.

3.2. Effect of red mud remediation of soils on plants

Remediation of metal-contaminated soils with red mud has been shown in a number of studies to reduce metal concentrations in plants consumed directly by humans or indirectly through fodder crops, with consequent benefits for human health [37, 49, 66, 75]. In the majority of these studies, conducted at both pot and field-scales, plant metal concentrations were reduced by more than 50% compared to plants grown in unamended soils (Tables 3 and 4).

Red mud has been shown to be a very effective amendment for reducing Cd, Pb and Zn uptake by plants grown in metal/metalloid-contaminated soils. Metal concentrations in plant tissues (rice (*Oryza sativa*) grains) decreased with increasing red mud application rates from 0.25 to 1.25% to contaminated soil [65]. Pea (*Pisum sativum* L.) and wheat (*Triticum vulgare* L.) plants grown on soils amended with red mud accumulated significantly lower amounts of Cd, Pb and Zn compared to plants grown in unamended soil [75]. Moreover, in the same study, red mud amendment increased the proportion of metal accumulation in the roots compared to the shoots of both plant species. The translocation factor (TF, metal concentration in shoot/metal concentration in root) for Cd, Pb and Zn in peas grown in red mud-amended soil was 0.086, 0.028 and 0.279, respectively, much lower than in peas grown in unamended soil (0.384, 0.052 and 0.825, respectively). Similar changes in metal translocation factors following red mud amendment were reported in studies using wheat

plants [75]. In contrast, in a pot experiment accumulation of Cu in corn (*Zea mays*) increased by 14% with the application of red mud, and there was no significant difference in Cd concentrations in plants grown in amended and unamended soil [37]. However, in a field experiment, Cd concentrations increased by more than 100% in both barley (*Hordeum vulgare* L.) grain and straw [45]. For vegetables, red mud could also play a positive role in reducing the plant metal content. Compared to unamended soil, the concentrations of As and metals in lettuce (*Lactuca sativa* L.) grown in soil amended with 2% red mud decreased by 32.8% (As), 83.5% (Cd), 35.4% (Pb) and 81.0% (Zn), compared to lettuce grown in unamended soil [66]. Metal contamination in fodder crops can indirectly affect human health as metals can be transferred through the food chain. To assess the long-term effectiveness of red mud amendment, red fescue (*Festuca rubra*) was harvested on three consecutive occasions at 120, 220 and 310 days after establishment. Analysis of the harvested shoots after each harvest showed that the red mud amendment continued to reduce plant uptake of Cd even after >300 days following application, with 38%, 73% and 70% reduction in concentration compared to plants grown in unamended soil, respectively [62].

Table 3. Pot experiments: effect of red mud amendment of metal-contaminated soils on metal concentrations in plants and plant biomass yield.

Red mud application rate (w/w) and red mud number in Table 1	Crop	Growth time (days)	Plant part assessed	Change in plant metal concentrations (%)	Change in biomass yield (%)	Reference
1%, 18	<i>Amaranthus hybridus</i> /Green amaranth	90	Shoot	Cd (-37)	NA	[62]
1%, 18	<i>Festuca rubra</i> /Red fescue	120	Shoot	Cd (-15)	NA	[62]
1%, 8	<i>Oryza sativa</i> /Rice	90	Grain	Cd (-58), Pb (-35), Zn (-25)	-2.8	[65]
2%, 16	<i>Lolium multiflorum</i> Lam. /Ryegrass	35	Shoot	As (-6) ^a , Cu (-31) ^a	-22 ^a	[52]
2%, 16	<i>Lactuca sativa</i> L. /Lettuce	42	Shoot	As (-26) ^a , Cu (-63) ^a	+143 ^a	[52]
2%, 9	<i>Lactuca sativa</i> L./Lettuce	NA	Shoot	As (-88), Cd (-97), Pb (-89), Zn (-97)	+413	[66]
2%, 9	<i>Miscanthus sinensis</i> /Eulalia grass	NA	Shoot Root	Cd (-6.0), Cu (-11), Pb (-32), Zn (-26) Cd (+14), Cu (+47), Pb (+29), Zn (+27)	NA NA	[67]
2%, 9	<i>Pteridium aquilinum</i> /Bracken	NA	Shoot Root	Cd (-16), Cu (-1.8), Pb (-11), Zn (+46) Cd (+84), Cu (+44), Pb (+0.4), Zn (+3.1)	NA	[67]
4%, 23	<i>Pisum sativum</i> L. /Pea	49	Shoot Root	Cd (-94), Pb (-77), Zn (-96) Cd (-73), Pb (-59), Zn (-89)	+80 +200	[75]
4%, 23	<i>Triticum vulgare</i> L./Wheat	49	Shoot Root	Cd (-94), Pb (-61), Zn (-89) Cd (-76), Pb (-52), Zn (-55)	+446 +497	[75]
5%, 13	<i>Zea mays</i> /Corn	100	Shoot	Cd (0), Cu (+14), Ni (-63), Pb (-77), Zn (-28)	+130	[37]
5%, 9	<i>Lactuca sativa</i> L./Lettuce	NA	Shoot	As (-62), Cd (-95), Pb (-59), Zn (-93)	+131	[66]
5%, –	<i>Chloris gayana</i> /Rhodes grass	84	Shoot	Pb (-73) ^a , Zn (-87) ^a	+860	[100]
10%, –	<i>Chloris gayana</i> /Rhodes grass	84	Shoot	Pb (-93) ^a , Zn (-93) ^a	+630	[100]

Notes: - decrease compared to the control, + increase compared to the control. 0 no change compared with the control. All increases or decreases are compared to plants grown on unamended contaminated soils. – in column 1 indicates red mud not listed in Table 1 as insufficient compositional information. NA, information not available. ^a % changes estimated from graphics presented in the references.

Table 4. Field experiments: effect of red mud amendment of metal-contaminated soils on metal concentrations in plants and plant biomass yield.

Red mud application rate (% w/w) and red mud number in Table 1	Crop	Growth time (days)	Plant part assessed	Change in plant metal concentrations (%)	Change in biomass yield (%)	Reference
0.5%, –	<i>Spinacia oleracea</i> L./Spinach	37	Leaf	Cd (-47)	+19	[54]
	<i>Lycopersicum esculentum</i> Mill./Tomato	133	Fruit	Cd (-49)	+7	
	<i>Brassica campestris</i> L./Chinese cabbage	NA	Leaf	Cd (-61)	+9	
	<i>Raphanus sativus</i> Linn./Radish	NA	Root	Cd (-66)	+22	
1%, 3	<i>Brassica rapa chinensis</i> /Pakchoi	40	Above ground	Cd (-26)	+64	[49]
			Root	Cd (-16)	NA	
1%, 15	<i>Hordeum vulgare</i> L./Barley	114	Grain Straw	Cd (+150), Pb (+5.4), Zn (-4.0) Cd (+134), Pb (-20), Zn (-9.6)	NA	[45]
1%, –	<i>Miscanthus sinensis</i> × <i>giganteus</i> /Giant miscanthus	770-1095	Root	Cd (-16), Pb (-56), Zn (-3.4)	+246 (Root+stem+leaf)	[102]
			Stem	Cd (-27), Pb (-42), Zn (-41)		
			Leaf	Cd (-56), Pb (-15), Zn (-11)		
		1095-1461	Root Stem Leaf	Cd (-37), Pb (-40), Zn (-11) Cd (-21), Pb (-63), Zn (-40) Cd (-38), Pb (-22), Zn (-62)	+156 (Root+stem+leaf)	
3%, 25	<i>Festuca rubra</i> /Red fescue	~300	Above ground	Cd (-67), Cu (-59), Pb (-19), Zn (-55)	+1965	[38]
		~640	Above ground	Cd (-73), Cu (-84), Pb (-84), Zn (-69)	+409	
5%, 25	<i>Festuca rubra</i> /Red fescue	~300	Above ground	Cd (-69), Cu (-66), Pb (-26), Zn (-80)	+3750	[38]
		~640	Above ground	Cd (-59), Cu (-77), Pb (-74), Zn (-59)	+378	

Notes: - decrease compared to the control, + increase compared to the control. All increases or decreases are compared to plants grown on unamended contaminated soils. – in column 1 indicates red mud not listed in Table 1 as insufficient compositional information. NA, information not available.

Despite the effectiveness of red mud amendment in reducing concentrations of metals and metalloids in plants grown in contaminated soils, plant material often still did not meet the relevant guideline limits for human consumption due to the highly contaminated soil on which they had grown [52]. For example, although the Cd concentration in wheat grain grown on red mud-treated soil decreased to 0.22 mg kg⁻¹ (dry weight basis, equivalent to 0.16 mg kg⁻¹ based wet weight) compared to 0.31 in the unamended soil [39], it still exceeds the maximum limit for Cd in cereals (0.1 mg kg⁻¹ wet weight) set by the European Commission [112]. Nevertheless, even though metal/metalloid concentrations in plants grown in red mud-amended soils might still exceed recommended concentrations in food stuffs and fodder crops, red mud amendment might help plants not destined for human consumption to grow in these contaminated soils and thus provide other ecosystem services, such as carbon sequestration, soil phytoremediation and reduction in soil erosion by water and wind.

In many studies, plant biomass increased due to soil remediation with red mud, resulting in a doubling of biomass in some plants compared with those growing in unamended contaminated control soil. Even though the Cu content of corn (*Zea mays*) was higher when grown in red mud-amended soil, plant biomass increased by 130% compared with the unamended soil [37]. Furthermore, in both pot and field experiments with 5% red mud application rate the biomass yield of red fescue (*Festuca rubra*) increased by more than 100% compared to the control [38]. However, Tian et al. [65] found the grain yield of rice (*Oryza sativa*) decreased with 1% w/w red mud addition. Similarly, in experiments with addition of 2% red mud, the biomass yield of ryegrass (*Lolium multiflorum* Lam.) was reduced compared to the control although the As and Cu concentrations both decreased in the plants [52]. These contrasting results may be attributed to a number of factors including: the variable response and tolerance of different plants to red mud constituents; differences in the nature of the soil undergoing remediation; and the effect of red mud on soil water balance and the availability of soil macronutrients, particularly phosphorus (P) [113], and micronutrients, such as manganese [39]. For example, red mud added at 5-50% w/w to a sandy soil significantly

increased soil water holding capacity at all addition rates [114]. In a study of the interaction between red mud and phosphate fertiliser additions to a sandy soil and subterranean clover (*Trifolium subterraneum*) yield, higher P application was required initially to maintain clover yield as a result of P sorption by freshly applied red mud [42]. However, an increase in clover yield response to further P addition 1 year after red mud application was attributed to reduced sorption of P arising from neutralisation of the red mud pH by the soil and also existing occupation of sorption sites with P.

3.3. Response of soil microbiological properties to red mud amendment of metal-contaminated soil

The influence of red mud on soil microbiological properties has been evaluated in only a limited number of studies during the past decade. A summary of relevant studies is shown in Table 5. Some of these reported no significant difference in microbial biomass between red mud-amended soil and the control soil (e.g. [52]). However, other studies have shown beneficial changes in soil microbiological properties as the result of red mud addition [50, 73-75]. These discrepancies may be partly attributed to the interaction between changes in soil chemical properties resulting from red mud addition and soil microbiological properties. For example, Garau et al. [50] reported significantly decreased TOC and increased water-soluble C, N, P, phenol and carbohydrate concentrations in soil from the vicinity of a former Pb-As mine 2 years after red mud addition, compared to the unamended control soil, giving rise to a priming effect due to red mud addition and stimulation of soil microbial growth and activity.

In more detail the microbial biomass-C has been reported to be significantly higher in red mud-amended soil (306 mg C kg⁻¹ soil dry weight) compared to the untreated soil (237 mg C kg⁻¹) [50] 2 years after red mud addition. In an experiment in which 3% red mud w/w was added to 10 kg microcosms of contaminated soil from near an abandoned mining site in Italy (principal contaminants As and Pb at 2105 and 714 mg kg⁻¹, respectively), the number of culturable heterotrophic bacteria increased 6-fold compared to the control soil after 6 months incubation at constant temperature, humidity and moisture [73]. A significant decrease in the number of heterotrophic fungi has been reported after addition of red mud to metal-contaminated soils in this study and others [74, 75]. These differing effects are attributed to lower pH values in the unamended soil favouring fungi and higher pH values in the amended soil due to red mud addition favouring bacteria [115]. The addition of red mud to the contaminated soil significantly influenced microbial populations and community composition. The microbial population from the red mud-amended soil showed a higher richness than the control soil and was dominated by Gram negative bacteria affiliated to *Ralstonia*, *Flavobacterium* and *Pedobacter* genera, whilst the control soils were dominated by Gram positive bacterial species, e.g. *Arthrobacter*, *Paenibacillus* and *Bacillus* species [74].

Table 5. Effect of red mud amendment of metal/metalloid-contaminated soils on soil properties and microbial activities.

Red mud application rate (% w/w) and red mud number in Table 1	Soil total metal concentration (mg kg ⁻¹)	Soil pH	Soil EC (%)	Soil total organic C (%)	Soil microbial biomass-C (%)	Change in dehydrogenase activity (%)	Change in urease activity (%)	Change in β -glucosidase activity (%)	Change in phosphatase (%)	Reference
2%, 9	As: 20.0, Cd: 2.5 Pb: 117, Zn: 233	Control: 5.22 Red mud: 8.10	+203	NA	NA	+139	+539	NA	-1.2	[66]
3%, 22	As: 2105, Cd: 18, Cu: 265, Pb: 714, Zn: 522	Control: 6.84 Red mud: 8.80	+64.0	-16.0	+65.1	+28	+726	-52.8	NA	[73]
4%, 23	Cd: 35, Pb: 3266, Zn: 1495	Control: 4.23 Red mud: 7.11	NA	-2.8	NA	+60	+215	-27.6	NA	[75]
4%, 22	As: 2428, Cd: 19, Pb: 556, Zn: 438	Control: 6.22 Red mud: 7.87	+51.2	-42.4	+22.7	+40	+1070	-11.1	-32.0 Alkaline phosphatase -8.9 Neutral phosphatase	[50]
5%, 9	As: 20, Cd: 2.5 Pb: 117, Zn: 233	Control: 5.22 Red mud: 9.35	+323	NA	NA	+46%	+546	NA	+39.3	[66]

Notes: - decrease compared with the control, + increase compared with the control. NA, information not available. All increases or decreases are compared to unamended contaminated soils.

The effect of red mud addition on soil microbial properties depends on the level of contamination in the soil being treated. Using *E. coli* and *P. fluorescens* biosensors, the greatest reduction in the toxicity of pore water in a pot experiment using contaminated soil from the vicinity of a Zn smelter (containing total Zn concentration 2920 mg kg⁻¹) [43] was reported to occur after 2% w/w addition of red mud compared to other amendments of lime and beringite [39]. When the biosensors were exposed to pore water from untreated soil their luminescence was less than 1% of the red mud treated soil probably due to the high concentration of Zn (81 mg l⁻¹) in the pore water, compared to <2 mg l⁻¹ Zn in the pore water of soil amended with red mud. In red mud-amended soil, soil microbiological parameters (respiration, urease, phosphatase, and dehydrogenase) were significantly negatively correlated with Ca(NO₃)₂-extractable trace element contents and also positively correlated with soil pH [46, 66]. The processes by which red mud amendment affects soil microbial properties is suggested to be not so much a direct effect of increasing soil pH, but rather that the increased soil pH enhances immobilisation of toxic trace elements through sorption, reducing their bioavailability and therefore the toxicity to soil microorganisms [46].

The addition of red mud to contaminated soil produces a wide range of biological responses from stimulation to inhibition of selected enzyme activities. The activity of β -glucosidase, which plays a major role in the soil C cycle, decreased significantly in soils treated with red mud, hence it may not be a useful indicator for assessing the recovery of metal-contaminated soil [50, 73]. Soil pH change might have been mainly responsible for this behaviour because it has been shown that β -glucosidase activity is pH-dependent, with a maximum activity at pH 5-6 [74, 75, 116]. In addition β -glucosidase activity in the unamended soil was strongly associated with fungi abundance, and may have been associated with decreased abundance of fungi in the red mud-amended soil [73].

Enzymes, such as urease and phosphatase, have been recommended as biochemical indicators of the quality of contaminated soils [117]. Soil enzyme activities can be inhibited by toxic trace elements through ionic competition with metallic enzyme cofactors, or by interacting with either active catalytic enzyme sites or potential enzyme substrates [66, 118]. Several studies have shown that red mud addition to contaminated soils significantly increased soil urease activity (Table 5). Urease activity was found to be positively correlated with soil pH, soil TOC and total N [75, 119, 120]. Phosphatase activity in soil was also reported to increase

by more than 90% in the presence of red mud over a 5-week incubation period whilst there was no significant increase in the control soil [121].

Dehydrogenase activity is also widely used to evaluate the metabolic activity of soil microbial communities and is considered a more sensitive indicator of the effects of metals on soil microbial properties than other soil parameters [122]. Increased dehydrogenase activity by 60% has been reported in red mud-amended soils compared to the unamended soil and has been attributed more to reduced metal bioavailability resulting from red mud addition rather than an increase in soil pH [74].

4. Summary and conclusions

Red mud is capable of immobilising PTEs in the majority of metal/metalloid-contaminated soils. One positive side effect of the use of red mud on contaminated soils could be the reduction of the vast volumes of red mud in storage. For example, the estimated production of red mud in China in 2015 was 88 million t a⁻¹ based on alumina production. Applying red mud at 3% w/w to the top 0.2 m soil in the 1.5 million ha of land in China contaminated by mining activities would use 122 million t, more than 1.3 times the red mud produced in 2015. Therefore, using red mud as a soil amendment would be an effective way to reduce the current storage. Based on the literature reviewed, a preliminary scheme is proposed for a decision tree to assess the suitability of red mud as an amendment for PTE-contaminated soil (Fig. 2). In applying this scheme it should be recognised that: (i) further studies, particularly at the field scale, will help to define critical thresholds, and (ii) site-specific risk assessments are required, to include, amongst other considerations, PTE mobility in the red mud and soil and site factors which might enhance mobilisation (discussed below).

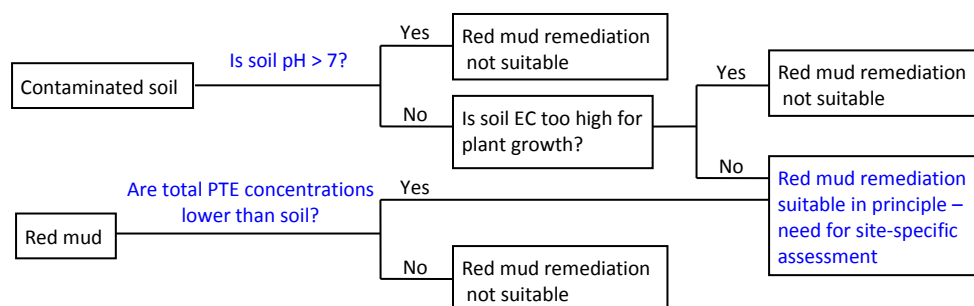


Fig. 2. Preliminary proposed scheme for assessing the use of red mud to remediate contaminated soil.

The key considerations arising from the literature for the use of red mud to remediate metal/metalloid-contaminated soil are summarised below.

(1) Fractionation studies have shown that metals in red mud are mainly associated with the less reactive phases, suggesting that they are not readily mobile under natural or even moderately acidic or reducing conditions. Red mud was found to be effective in reducing metal/metalloid mobility with the conversion of mobile fractions to the Fe/Mn oxides fraction. The immobilisation of metals by red mud addition to contaminated soils is related to a number of mechanisms. These include increased metal adsorption, due to the increasing negative surface charge of soil, and precipitation of metal hydroxides and carbonates at high pH, and also surface complexation with Fe oxides and formation of inner sphere complexes

with Fe and Al oxides and hydroxides. Acidification of red mud-amended soil may cause increased metal release from the amended soil since the mobility of metals is closely related to pH. Besides acidification, remobilisation could also occur due to other environmental changes (such as water logging which can create reducing conditions, resulting in the release of PTEs immobilised by Fe/Mn oxides). More information is required about the long-term stability of PTEs fixed when red mud is added to contaminated soils, particularly in field experiments which have been rare.

(2) In some cases, red mud addition was less effective in immobilising As and Cu compared to other metals. An appropriate pre-treatment method, such as neutralising red mud with seawater, may be helpful to improve the fixation of Cu in amended soils. Although there is the possibility of increasing the remediation effectiveness of red mud through pre-treatment, more research is required on how different pre-treatment methods influence the effectiveness of red mud for remediation of contaminated soil.

(3) In developing future policy there is a need to consider the remediation effectiveness and possible risks related to the common characteristics of red mud. In addition to setting maximum permissible concentrations of PTEs in red mud according to the pH of the contaminated soil and its existing PTE concentrations, maximum permissible average annual rates of addition of PTEs over the long-term should be limited to avoid negative effects caused by accumulated elements from red mud. There is currently a lack of pilot studies and field applications which could further enhance the establishment of guidelines. Best practice examples could provide evidence for decision making for red mud application on a site-specific basis.

(4) High application rates (> 5% w/w) of red mud are possibly not practicable and may lead to new soil contamination problems, including high salinity mostly caused by the high Na content of red mud. Red mud should not be used for remediation when its metal content is higher than in the contaminated soil, despite the high metal fixation ability of red mud, in order to avoid increasing metal/metalloid concentration in the amended soil. The consideration of red mud as an amendment for contaminated soil should always be a risk-based decision, in which factors such as the target metals to be immobilised and the soil pH are assessed carefully.

(5) Due to the risk of contamination entering the human food chain, red mud should not be used to remediate contaminated soils for food or fodder crop production. However, red mud amendment might help plants not destined for human consumption to grow in these contaminated soils. Red mud amendment of contaminated soils will have wider benefits for ecosystems and the environment in reducing the mobility of PTEs and their transfer by water and wind.

(6) This review has focussed on the effectiveness and potential risks of the characteristics of red mud for remediating contaminated soil. In addition to the PTE content and high salinity of red mud, radioactivity is another consideration in the application of red mud, although there is very limited information on this topic. Moreover, the economics of using red mud in this manner also require investigation. Although red mud as an industrial waste is cheap, the transport and application costs may not be, especially if the location of red mud production is distant from the contaminated soil. A combined economic and technical assessment should be carried out to better address the engineering application of red mud.

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